Appl. No. 10/092,792
Amdt. dated August 10, 2004
Reply to Office Action of June 29, 2004

REMARKS

Applicants respectfully request entry of this Amendment and reconsideration of this application, as amended. Claims 1-7, 9 and 11-18 remain in the application. Non-elected claims 19-42 have been cancelled. In addition, claims 8 and 10 have been cancelled. Support for the amendment to claim 1 can be found in claim 8, as originally filed.

Restriction Requirement

Applicants note the restriction requirement made final in the last Office Action and confirm election of Group I, claims 1-18. Non-elected claims 19-42 have been cancelled in order to facilitate the prosecution of this case.

Rejections Under 35 USC 112

Claims 1-18 have been rejected under 35 U.S.C. 112, second paragraph, as being indefinite for failing to point out and distinctly claim the subject matter which Applicants regard as the invention. The terms "type" and "types" have been deleted from the claims, thus obviating the above rejection.

The dependency of claim 11 has been changed from claim 6 to claim 7 in order to provide proper antecedent basis for "the reflection peak in the ...range." In addition, the dependency of claim 9 has also been changed.

Rejections Under 35 USC 102/103

Claims 1-18 have been rejected under 35 U.S.C. 102(b) as anticipated by or, in the alternative, under 35 U.S.C. 103(a) as obvious over either U.S. Patent 5,324,493 to Mueller et al. (Mueller) or WO 98/15496. Reconsideration is respectfully requested.

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Claim 1, as currently amended, recites a silicoaluminophosphate molecular sieve having an X-ray diffraction pattern characterized by the absence of peaks in the 9.8 to 12 (2θ) range. The diffraction patterns of the aluminophosphates and silicoaluminophosphates prepared by Mueller contain at least the interplanar spacings (d in Angstrom) stated in Table 1 in column 3 of Mueller. The Mueller reference clearly discloses a peak between 9.5-9.8 (2θ), which is excluded by the amended claim 1.

Claim 1 also recites a silicoaluminophosphate molecular sieve comprising at least one intergrown phase of molecular sieves having AEI and CHA frameworks. There is no disclosure of either an AEI or a CHA framework in Mueller. In fact, Mueller discloses an AEL structure. AEI/CHA molecular sieves have a different structure type than the structure type of the Mueller molecular sieves. These different structure types are discussed in the Atlas of Zeolite Structure Types (copies of the relevant pages are attached for the Examiner's convenience).

All the materials disclosed in WO 98/15496 exhibit an X-ray reflection peak at 10.4-10.6 degrees (2θ), while claim 1, as currently amended, excludes the presence of such a reflection in the X-ray diffraction spectrum of the claimed silicoaluminophosphate molecular sieve.

In view of the above, it is respectfully submitted that Mueller and WO 98/15496, both alone and in combination, fail to disclose or suggest Applicants' invention as now claimed. Withdrawal of the rejections based on these references is therefore requested.

Claims 1-18 have been rejected under 35 U.S.C. 102 (e) as anticipated by or, in the alternative, under 35 U.S.C. 103 (a) as obvious over U.S. Patent 6,294,493 to Strohmaier et al. (Strohmaier) which teaches silicoaluminophosphates having an AEL structure and a high

silica/alumina ratio. Examples 1-7 disclose the preparation of ECR-42 and Example 8 discloses preparation of SAPO-11.

Instant claim 1 recites a silicoaluminophosphate molecular sieve comprising at least one intergrown phase of molecular sieves having AEI and CHA frameworks. There is no disclosure of either an AEI or a CHA framework in Strohmaier. In fact, Strohmaier discloses an AEL structure. AEI/CHA molecular sieves have a different structure type than the structure type of the Strohmaier molecular sieves. These different structure types are discussed in the Atlas of Zeolite Structure Types (copies of the relevant pages are attached for the Examiner's convenience).

Thus, the reference lack the positive recitation required of an anticipating reference or any teaching of obviousness. In view of the above, withdrawal of the rejection is respectfully requested.

Obviousness Type Double Patenting

Claims 1-18 have been provisionally rejected under the judicially created doctrine of obviousness-type double patenting as being unpatentable over claims 1-31 of copending Application Serial No. 09/924,016. According to the Examiner, although the conflicting claims are not identical, they are not patentably distinct from each other because the instant claims are broader than the claims recited in Application Serial No. 09/924,016. However, the instant claims now been narrowed and so are no longer broader than those of Application Serial No. 09/924,016. Moreover, since Application Serial No. 09/924,016 has not issued, it is respectfully submitted that this rejection is not yet ripe. If required, a terminal disclaimer will be filed when the present application is otherwise in order for allowance.

In view of the foregoing remarks, it is respectfully submitted that the present claims describe a silicoaluminophosphate molecular sieve which meets the requirements of

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patentability. Applicants therefore respectfully request that a timely Notice of Allowance be
issued in this case.

Any comments or questions concerning the application can be directed to the
undersigned at the telephone number given below.

Respectfully submitted,

Date: August 10, 2004   By: _____

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SYSTEMATIC RELATIONSHIPS BETWEEN THE STRUCTURES OF CHA, AEI AND KFI

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SUMMARY

Identification of families of structure types and the systematic way the structures are related
might be used as a tool for the identification of new structure types. Our investigation has
resulted in the discovery that there is a systematic relationship between the known structures
chabazite (CHA), $AlPO_4$-18 (AEI), ZK-5 (KFI) and a fourth closely related theoretical
variant.

INTRODUCTION

One interesting aspect of zeolite chemistry is the number and variety of structure types and
the regularity with which new and unique structures appear on the scene. The solution of these
new structures has in many cases relied on model-building and attempts to relate
characteristics of pore dimensions and unit cell parameters to known frameworks[1]. An
important basis for this approach is the identification of families of structure types and the
systematic way they are related.

RESULTS AND DISCUSSION

Our investigation into materials related to chabazite and the recently solved $AlPO_4$-18[2] has
resulted in the discovery that there is a systematic relationship of these two structures to a
third known framework type ZK-5. The now obvious inter-relationship of these three
framework types also leads us to identify a fourth closely related theoretical variant, with the
four structures forming the complete set of end-members for an infinite series of intergrowth
structures of which the fundamental repeating unit is the familiar double six-ring (D6R). An
independent study by A. Simmen[3] has also noted the existence of the related theoretical
structure. An additional interesting feature of these four structures is the wide variety of

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compositions which they encompass. This ranges from the purely aluminosilicate (chabazite, ZK-5) to aluminophosphate (AlPO$_4$-18) to silica-aluminophosphate (SAPO-34), the chabazite framework type being the only one that is currently found to exist in both zeolite and aluminophosphate form.
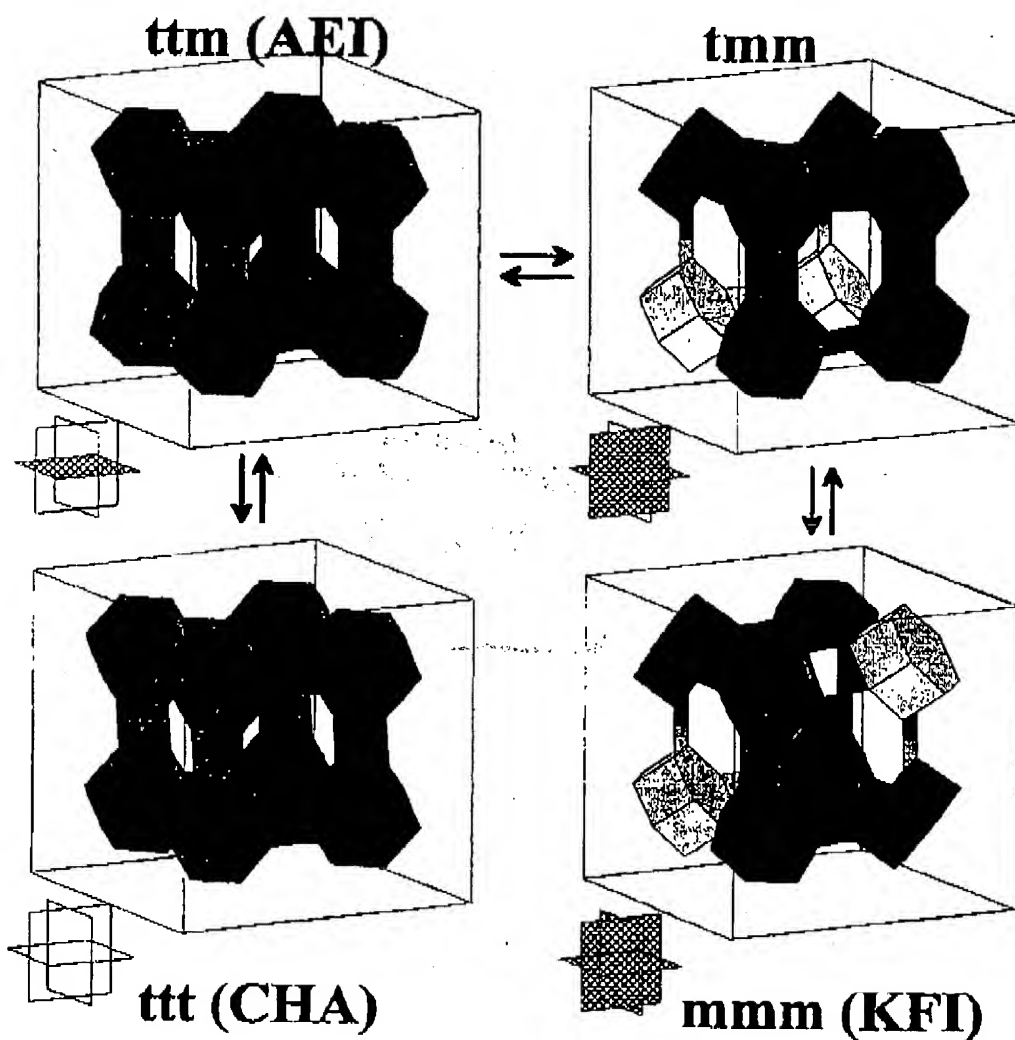

Figure 1. Illustration of the systematic relations beween these four structures.

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The systematic relations of these four structures is schematically illustrated in Figure 1. The structure of ZK-5 can be seen to be composed of a series of D6R units tilted with respect to the three orthogonol crystallographic axes. Each D6R unit is related to all connected neighbouring units by mirror symmetry, so that mirror planes orthogonal to all three crystallographic directions (mmm) can be imagined to generate the complete unit cell contents of 8 D6R units. The structure of chabazite can be described in the same manner, however, all adjacent connected D6R units are related by translational symmetry (ttt) and thus are all tilted in the same direction, as opposed to ZK-5 in which they alternate between tilting towards and away from each other. Thus in the chabazite case, translational operators along all three crystallographic axes generate the 8 D6R units represented in the figure. Due to the hexagonal symmetry of the framework, the smallest unit cell describing the structure actually contains only one D6R unit. AlPO4-18, in contrast to ZK-5 and chabazite, contains a mixture of the translational and mirror operators (ttm). As is evident from the figure, only one mirror plane is present, orthoganol to the c axis, whereas the rest of the D6R units are generated along the a and b directions by translational symmetry. The smallest unit cell describing the framework is now orthorhombic and contains two D6R units. The final end-member, the theoretical variant, contains two mirror planes orthogonal to the a and b axes, with D6R units related by translational symmetry only along the c direction (tmm). In this case the smallest unit cell describing the structure contains 4 D6R units and in its highest symmetry is described by the tetragonal space group P4/nmm. Optimised coordinates for this new structure are presented in Table 1.

Table 1. Optimised coordinates from energy minimisation calculations for the theoretical end-member (tmm)

a	= 18.30462,	b	= 18.30462,	c	= 9.23704,
alpha	= 90.00000,	beta	= 90.00000,	theta	= 90.00000
Space group	= P4/nmm				

Atom	X	Y	Z
SI1	-0.20301	-0.58409	-0.15960
SI2	-0.31571	-0.58374	0.08825
SI3	0.30424	-0.68444	-0.33635
O1	-0.18731	-0.50000	-0.19658
O2	0.33330	-0.50000	0.12050
O3	0.24195	-0.59313	-0.00462
O4	-0.12640	-0.62640	-0.15461
O5	-0.25539	-0.61645	-0.28380
O6	-0.38351	-0.61649	0.00000
O7	-0.30554	-0.62397	0.24014
O8	0.24113	-0.74113	0.32349
O9	0.32979	-0.67021	0.50000

Since the series of structures are so closely related in geometry, it was interesting to compare the relative stabilities of the end-members. We have carried out energy minimisation calculations for the four structures described here and a number of intermediate intergrowths,

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in order to provide some initial assessment of the differences in their stabilities on the basis of their lattice energies. Similar calculations have been carried out on two of the polymorphs of zeolite beta[4]. In these studies, all structures were assumed to be pure silica with the minimisations allowing complete relaxation of the unit cells[5]. Literature values of crystallographic coordinates were used for known structures. For the theoretical variant and intergrowths the coordinates were calculated and initially optimised using DLS-76[6]. Comparison of the lattice energies are presented in Figure 2 along with energies of a number of other well known systems, with alpha-quartz been used as a baseline. Only small differences in the energies of the four end-members are apparent with the structures of chabazite and AlPO$_4$-18 having the lowest energies, whereas ZK-5 and the new structures have near identical lattice energies. Results from the calculations for a number of the ordered intergrowths of pairs of the end-members (CHA-AEI, AEI-tmm) also show very similar energies to the pure phases.

Table 2.
d and intensity values for the
hyptetical structure TMM.

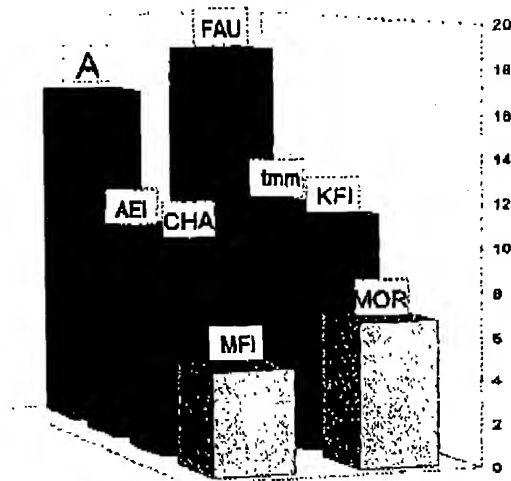| d-value	Int
12.94	10
9.16	100
8.24	22
7.51	1
6.49	7
5.79	9
5.29	27
5.08	17
4.61	2
4.57	2
4.45	6
4.31	9
4.09	8
4.02	2
3.90	5
3.74	3
3.68	9

Figure 2. Comparison of the lattice energies of the four structures along with energies of a number of other well known systems. The lattice energy of alpha-quartz has been used as a baseline. The METAPOCS code has been used in the minimisations which have been carried out at constant pressure and 0 K.

The simulated powder XRD patterns of the four end-member phases are presented in Figure 3 and the tabulated d and intensity values for the tmm structure are supplied in Table 2. It is apparent that the XRD patterns are very similar, for example, a physical mixture of AlPO$_4$-

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18 and ZK-5 would be very difficult to distinguish from the pattern derived from the theoretical structure (tmm). In this case the only diagnostic lines would be those at 13 and 17° if they could be resolved. The correct recognition of these small differences could be quite crucial in determining the existance of mixtures or the presence of the new phase.

The existance of structures which are end-members of an infinite inter-growth system along one crystallographic axes (OFF/ERI[7], FAU/HEX[8]) or two crystallographic axes (ZSM-5/ZSM-11[9,10], Zeolite beta[11]) is known. For many of these systems, the intimate relation between the end-member phases has
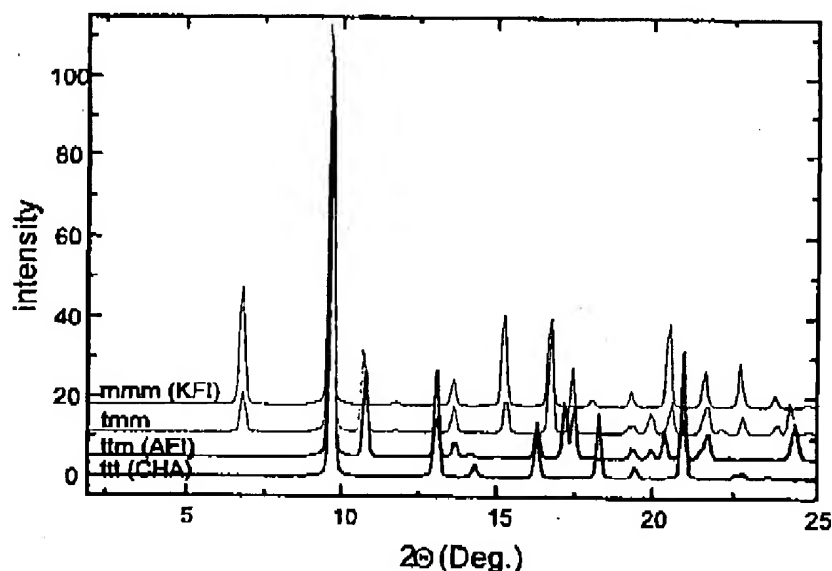

Figure 3. Simulated powder XRD patterns of the four end-member phases.

resulted in difficulties in the synthesis of a pure phase of either of the end-members in the absence of stacking faults. This is particularly evident for zeolite beta which has not so far been obtained as a pure phase due to the near random nature of the intergrowths. Such problems do not apparently apply to the CHA/AEI/ZK-5 system which to our knowledge have never been reported as exhibiting intergrowth structures.

The identification of the intergrowths in the powder XRD is likely to be even more difficult than of the physical mixtures. Treacy and Newsam [12] have developed a computer program (DIFFaX) to simulate diffraction patterns of intergrown phases. This work shows that the pattern derived from such intergrowths is not a linear combination of the patterns of the end members. It is therefore necessary to perform the calculations for the CHA/AEI/ttm/ZK-5 system as an aid to identifying the new phases. Figure 4 presents an example of the DIFFaX

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calculation for the CHA/AEI series, going from pure chabazite to pure AlPO$_4$-18 assuming a random distribution of the layers.
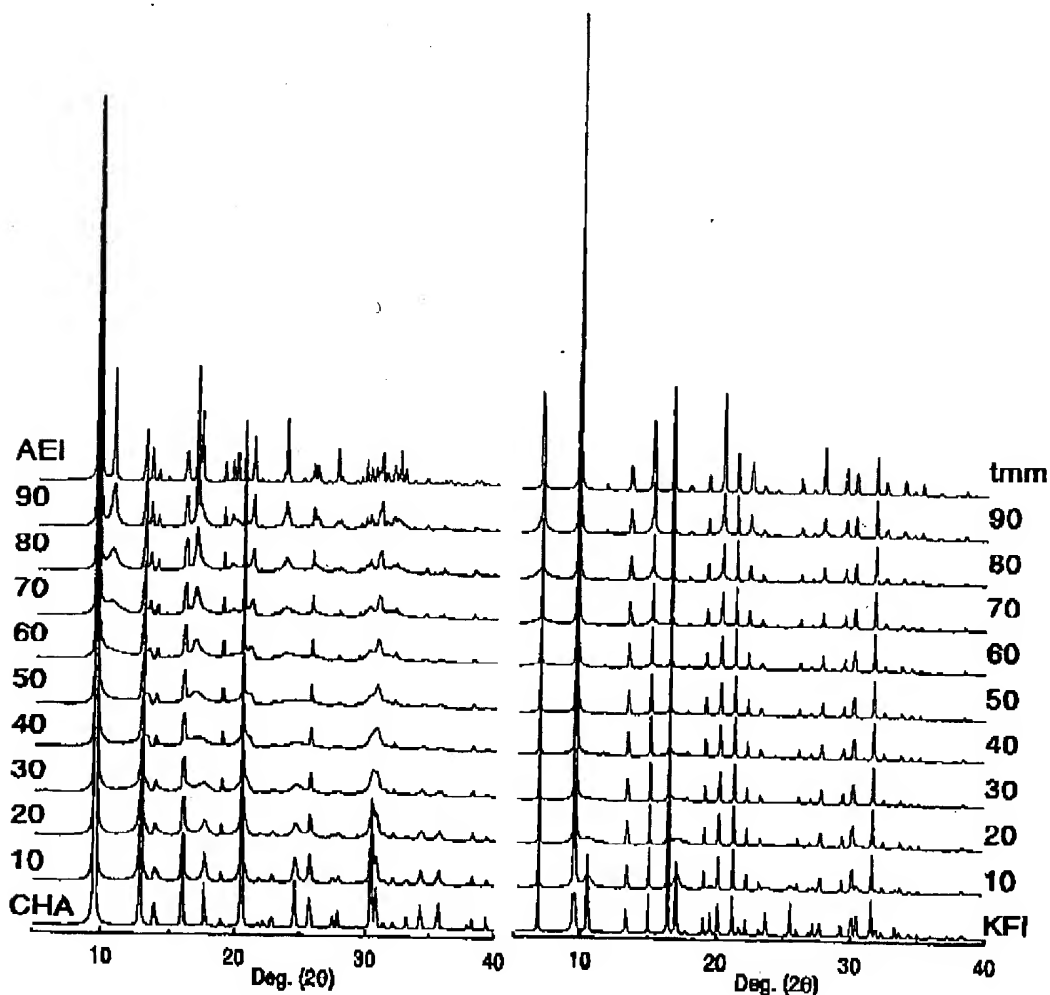

Figure 4. Intergrowths in the CHA/AEI series, going from pure chabazite to pure AlPO$_4$-18 assuming a random distribution of the layers.

Figure 5. Intergrowths in the tmm/KFI series, going from the pure tmm to pure ZK-5 assuming a random distribution of the layers.

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One of the most interesting aspects of identifying families of closely related structures such as the CHA/AEI/ttm/KFI system is the possiblity to define a synthesis strategy that forms a systematic approach to the synthesis of new phases, particularly in combination with the detailed simulation of the predicted XRD patternsof the new phase and intergrowths.

Such a systematic study is being carried out in our lab and initial results show that chabazite and ZK-5 can co-crystallize from the same gel composition. Crystallization at 150°C results in the formation of a very pure chabazite phase, while the same gel composition crystallized at 90°C results in a physical mixture of chabazite and ZK-5, with ZK-5 being the main component. To our knowledge, the co-crystallization of these two phases has not been reported.

In the aluminophosphate system, recent work by J.Jänchen et al.[13] has now shown that reducing the amount of silica in the gel for the synthesis of a standard SAPO-34 material (CHA framework) results in the change from SAPO-34 to AIPO$_4$-18 under a critical concentration of silica. This initial synthesis work thus shows that all the three known phases can co-crystallize from the same gel compositions.

CONCLUSION

The previously unreported close relationship between the chabazite and ZK-5 frameworks has been identified. AIPO$_4$-18 and a new hypothetical structure (tmm) are also identified as intermediate end-members of lower symmetry. These four phases define a three-dimensional intergrowth system, previously unknown for zeolites. This system forms the basis for a systematic synthesis strategy towards isolating and identifying the new phase and intergrowths. Initial synthesis results already indicate the co-crystallization of the three known phases from the same gel compositions.

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